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AMINO-SUBSTITUTED SULFONIUM SALTS; SYNTHESIS AND STEREOCHEMISTR--ETC(U)

MAY 78 A H COWLEY, D J PAGEL, M L WALKER

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6 Amino-Substituted Sulfonium Salts;
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The amino-substituted sulfonium cations, $[(\text{Me}_2\text{N})\text{SF}_{3-x}]^+$, $x=1,2$, have been prepared by treating the appropriate ^x fluorosulfur- ane, $(\text{Me}_2\text{N})\text{SF}_{4-x}$, with BF_3 , PF_5 , or AsF_5 as fluoride ion acceptor in SO_2 solution at -60° to -65°C . The cation, $[(\text{Me}_2\text{N})_3\text{S}]^+$, has been synthesized via the reaction of SF_4 with $(\text{Me}_2\text{N})_3\text{B}$ in SO_2 solution at low temperature. The course of the latter reaction has been followed by ^1H and ^{19}F NMR spectroscopy.		

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The stereochemistry of $[\text{Me}_2\text{NSF}_2]^+$ has been investigated by variable temperature ^1H , ^{19}F , and ^{13}C NMR. These data establish that in the ground state $[\text{Me}_2\text{NSF}_2]^+$ is isostructural with the isoelectronic aminophosphine, Me_2NPF_2 . The barrier to N-S torsion in $[\text{Me}_2\text{NSF}_2]^+$ is 14.7 kcal/mole.

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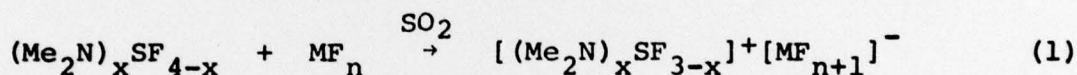
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Amino-Substituted Sulfonium Salts; Synthesis and Stereochemistry

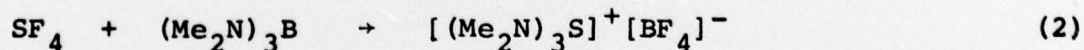
Sir:

Amino-substituted sulfonium cations, $[(R_2N)_xSF_{3-x}]^+$, $x = 1, 2, 3$ are isoelectronic with aminophosphines and, consequently, their stereochemistry, reactivity, and ligand behavior are of significant potential interest.

We find that the syntheses of the $[Me_2NSF_2]^+$ (1) and $[(Me_2N)_2SF]^+$ (2) cations can be accomplished in high yields by treatment of the appropriate fluorosulfurane with a fluoride ion acceptor such as BF_3 , PF_5 , or AsF_5 in SO_2 solution at -60 to $-65^\circ C$.



This is a similar approach to that used¹ for the synthesis of $[SF_3]^+[BF_4]^-$. However, since the fluorosulfurane, $(Me_2N)_3SF$, is unknown it was necessary to develop a novel synthesis for the completely amino-substituted cation, $[(Me_2N)_3S]^+$ (3). After several unsuccessful attempts to prepare the latter by treating 1 or 2 with dimethylamide anion, we discovered that the reaction of SF_4 with $B(NMe_2)_3$ affords high yields of 3 as its tetrafluoroborate salt

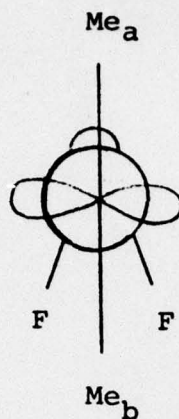


Typically, an equimolar mixture of SF_4 and $(Me_2N)_3B$ in SO_2 solution is allowed to warm slowly from -196° to $+10^\circ C$. Removal of the SO_2 and trace quantities of volatiles in vacuo afforded white, solid $[(Me_2N)_3S]^+[BF_4]^-$, mp 110° (decomp).² The reaction of SF_4 and $(Me_2N)_3B$ can be followed by NMR spectroscopy. Immediately after

warming to -60°C ^1H peaks corresponding to $\underline{1}$ (triplet, δ 3.18, $J_{\text{FSNCH}} = 7.5$ Hz), $\underline{2}$ (doublet, δ 2.95, $J_{\text{FSNCH}} = 7.0$ Hz) and $\underline{3}$ (singlet, δ 2.55) and $(\text{Me}_2\text{N})_3\text{B}$ are clearly discernible. The resonances corresponding to $\underline{1}$, $\underline{2}$, and $(\text{Me}_2\text{N})_3\text{B}$ decrease with time and that of $\underline{3}$ increases until, after 20 min at ambient temperature, all that remains is the singlet resonance of $\underline{3}$. ^{19}F spectra³ taken in the early stages of the reaction confirm the presence of SF_3^+ (singlet, -19 ppm), $\underline{1}$ (septet, -16.0 ppm, $J_{\text{FSNCH}} = 7.5$ Hz), $\underline{2}$ (multiplet, $+15.6$ ppm, $J_{\text{FSNCH}} = 7.0$ Hz) and, in addition, exhibit four poorly resolved "quartet" resonances which we attribute to BF_4^- (143.5 ppm, $J_{11_{\text{BF}}} = 2$ Hz), $[\text{Me}_2\text{NBF}_3]^-$ (153 ppm, $J_{11_{\text{BF}}} = 20$ Hz), $[(\text{Me}_2\text{N})_2\text{BF}_2]^-$ (155 ppm, $J_{11_{\text{BF}}} = 18$ Hz), and $[(\text{Me}_2\text{N})_3\text{BF}]^-$ (156 ppm, $J_{11_{\text{BF}}} = 17$ Hz).⁴ As time elapses the resonance due to BF_4^- grows at the expense of the other three. To accommodate the foregoing observations we postulate that the initial step in the reaction is F^- abstraction by $(\text{Me}_2\text{N})_3\text{B}$ to form $[(\text{Me}_2\text{N})_3\text{BF}]^-$ and SF_3^+ , the latter undergoing $\text{F}^-/\text{Me}_2\text{N}^-$ exchange with either $(\text{Me}_2\text{N})_3\text{B}$ or $[(\text{Me}_2\text{N})_x\text{BF}_{4-x}]^-$. In support of this postulate we find that (a) the AsF_6^- salts of SF_3^+ , $\underline{1}$, and $\underline{2}$ undergo rapid reaction with $(\text{Me}_2\text{N})_3\text{B}$ to afford $\underline{3}$, and (b) the sulfurane $(\text{Me}_2\text{N})_2\text{SF}_2$ does not react with $(\text{Me}_2\text{N})_3\text{B}$ in this temperature range.

The stereochemistry of aminosulfonium cations has been investigated by dynamic NMR. For example, below -30° the ^1H spectrum of $\underline{1}$ consists of two overlapping triplets which we attribute to two Me environments (Me_a , δ 3.95, $J_{\text{FSNCH}_a} = 9.5$ Hz; Me_b , δ 3.86, $J_{\text{FSNCH}_b} = 5.5$ Hz).⁵ This deduction is confirmed by the presence of two singlets in the ^{13}C spectrum (Me_a , 41.2 , and Me_b , 36.7 ppm).^{3,5} Under the same conditions the ^{19}F spectrum comprises a sixteen line spectrum which is

due to the coupling of the two Me groups to two equivalent F ligands. Taken collectively, the low temperature NMR data establish structure 4 for 1, and thereby demonstrate that aminosulfonium cations and amino-



4
phosphines are isosteric. Upon warming to -15° the ^1H spectrum collapses and emerges as a triplet, while the ^{13}C and ^{19}F spectra become a singlet (39.3 ppm) and a septet (-16.0 ppm, $J_{\text{HCNSF}} = 7.5$ Hz), respectively. These spectral changes are attributed to rotation around the N-S bond becoming rapid on the NMR time scale. Computer line shape analyses of the ^1H dynamic NMR indicate that the barrier to N-S rotation in 1 is 14.7 kcal/mole. This result implies that the N-S torsional barriers in aminosulfonium cations are significantly larger than the N-P barriers of the corresponding aminophosphines.⁷ Thus, aminosulfonium salts might find use as models for aminophosphine stereochemistry in cases where, because of low N-P torsional barriers, considerable doubt persists regarding the ground state geometry.

The coordination chemistry of aminosulfonium cations is under active investigation and will be reported in subsequent publications.

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References and Notes

- (1) (a) N. Bartlett and P. L. Robinson, Chem. Ind. (London), 1351 (1956); (b) N. Bartlett and P. L. Robinson, J. Chem. Soc., 3417 (1961); (c) F. Seel and O. Detmer, Angew. Chem., **70**, 163 (1958); (d) F. Seel and O. Detmer, Z. Anorg. Allg. Chem., **301**, 113 (1959).
- (2) A satisfactory elemental analysis and ir spectrum was obtained for $[(\text{Me}_2\text{N})_3\text{S}]^+[\text{BF}_4]^-$.
- (3) ^{19}F chemical shifts in ppm relative to external CCl_3F ; ^{13}C chemical shifts in ppm relative to external Me_4Si .
- (4) The ^{19}F chemical shift and ^{11}B - ^{19}F constant of $[\text{BF}_4]^-$ have been shown to be markedly dependent on concentration, and on the nature of the cation and solvent. See R. Hague and L. W. Reeves, J. Phys. Chem., **70**, 2753 (1966), and references therein. Presumably, the same is true for the "mixed" anions, $[(\text{Me}_2\text{N})_x\text{BF}_{4-x}]^-$.
- (5) In aminophosphines the Me protons cis to the phosphorus lone pair (Me_a) appear at lower field than those which are trans to the phosphorus lone pair (Me_b). Furthermore, the Me_a protons are more strongly coupled to phosphorus than the Me_b protons. A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, J. Am. Chem. Soc., **92**, 1085 (1970). Subsequently, the ^{13}C chemical shifts of Me_a and Me_b were found to be in the order $\text{Me}_a > \text{Me}_b$. M.-P. Simonnin, R.-M. Leguan, and F. W. Wehrli, J. Chem. Soc. Chem. Commun., 1204 (1972).
- (6) The isoelectronic aminophosphine, Me_2NPF_2 , has been shown to possess structure 4 by low-temperature X-ray crystallography. E. D. Morris and C. E. Nordman, Inorg. Chem., **8**, 1673 (1969).
- (7) The N-P torsional barrier of the isoelectronic species, Me_2NPF_2 , is too small to be measured by dynamic NMR. For aminophosphines with more bulky substituents the N-P torsional barriers fall typically in the range 8-10 kcal/mole. See A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, J. Am. Chem. Soc., **92**, 5206 (1970), and references therein. The N-P torsional barrier of Me_2NPF_2 has been estimated to be 2.8 kcal/mole by the CNDO/2 method. M.-C. Bach, C. Brian, F. Crasnier, J.-F. Labarre, C. Leibovici, and A. Dargelos, J. Mol. Structure, **17**, 23 (1973).

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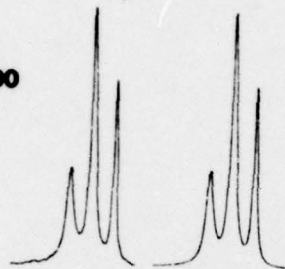
FIGURE CAPTION

Figure 1. Experimental (left) and computer-simulated ^1H NMR spectra of $[\text{Me}_2\text{NSF}_2]^+$ (1). The experimental spectra were obtained in SO_2 solution.

T=30°C
K=1580_{sec}⁻¹



T=0
K=100



T=-14
K=27.4



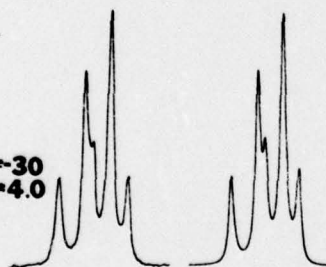
T=-16
K=21.2



T=-21
K=11.5



T=30
K=4.0



T=-40
K=1.0

